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Graph-theoretical Formula for Ring Currents Induced in a Polycyclic Conjugated System

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Synopsis. A graph-theoretical formula was derived for ring currents induced in a polycyclic conjugated system by a uniform magnetic field. Two advantages of this formula are that ring currents can be evaluated by inspecting a geometry of a conjugated system, and that they can be attributed to the individual π-electron rings.

In previous papers[1-6] we developed the theory of London (or ring-currents) diamagnetism[7-9] using graph-theoretical terms. This approach was found to be best suited for analyzing magnetic properties of a polycyclic conjugated system in conjunction with its structural features. We now extend our graph theory to uncover geometrical aspects of ring currents induced in a polycyclic system by a uniform magnetic field. Ring currents themselves were first formulated by Pople and McWeeny in 1958.[9-11]

We clarified before[2] that London (or ring-currents) susceptibility of a polycyclic conjugated system G, χ_G, can be partitioned exactly among the constituent π-electron rings, namely,

$$\chi_G = \sum_{i}^{G} \chi_i, \tag{1}$$

where χ_i is a susceptibility contribution from the ith π-electron ring, and i runs over all π-electron rings defined in Sachs' sense.[12] Explicitly, χ_i is expressed as[2]

$$\chi_i = -4\left(\frac{e}{c\hbar}\right)^2 \beta S_i^2 \sum_{j=1}^{n} \frac{P_{G-r_i}(X_j)}{P_G'(X_j)}. \tag{2}$$

Here, $P_G(X)$ is a characteristic polynomial for G; $P_G'(X)$ is a first derivative of $P_G(X)$ with respect to X; X_j is the jth largest root of the equation $P_G(X)=0$, *i.e.*, the jth orbital energy given relative to the carbon Coulomb integral and in units of β; n denotes the highest occupied orbital; r_i is the ith π-electron ring; G-r_i is a subsystem of G, obtained by deleting from G the ith π-electron ring and all π bonds incident to it; S_i is an area of the ith π-electron ring; and e, c, and $\hbar$ are the standard constants with these symbols.

The external magnetic field H provokes an induced moment M_G opposing it and given by the expression:

$$M_G = \chi_G H = \sum_{i}^{G} \chi_i H. \tag{3}$$

We define a partial moment of the ith π-electron ring by

$$M_i = \chi_i H. \tag{4}$$

Our hypothesis is that M_i arises from an induced ring current I_i circulating around the ith π-electron ring, *i.e.*,

$$M_i = \frac{I_i S_i}{c}. \tag{5}$$

The assumed ring current I_i is then expressible as

$$I_i = \frac{c\chi_i H}{S_i} = -4\frac{e^2}{c\hbar^2}\beta S_i H \sum_{j=1}^{n} \frac{P_{G-r_i}(X_j)}{P_G'(X_j)}. \tag{6}$$

When there are degenerate orbitals in G, Eq. 2 cannot be applied to them. We instead verified that four π electrons in doubly degenerate orbitals contribute to χ_i by the amount:[2]

$$\Delta\chi_i = -4\left(\frac{e}{c\hbar}\right)^2 \beta S_i^2 \times \frac{U(X_{j*})P_{G-r_i}'(X_{j*}) - U'(X_{j*})P_{G-r_i}(X_{j*})}{U(X_{j*})^2}, \tag{7}$$

where X_{j*} is a degenerate orbital energy, and

$$U(X) = \frac{P_G(X)}{(X-X_{j*})^2}. \tag{8}$$

Owing to Eq. 7, we can still define a partial moment for each π-electron ring. A ring current induced in benzene, I_0, is calculated as

$$I_0 = -\frac{2}{9}\frac{e^2}{c\hbar^2}\beta S_0 H, \tag{9}$$

where S_0 is an area of the benzene ring.

Finally, a ring current induced in a given π-electron ring of a polycyclic system is estimated in units of I_0 as

$$\frac{I_i}{I_0} = 18\frac{S_i}{S_0}\sum_{j=1}^{n}\frac{P_{G-r_i}'(X_j)}{P_G'(X_j)}. \tag{10}$$

Ring currents thus calculated for all π-electron rings of four compounds are presented in Fig. 1. We assumed that

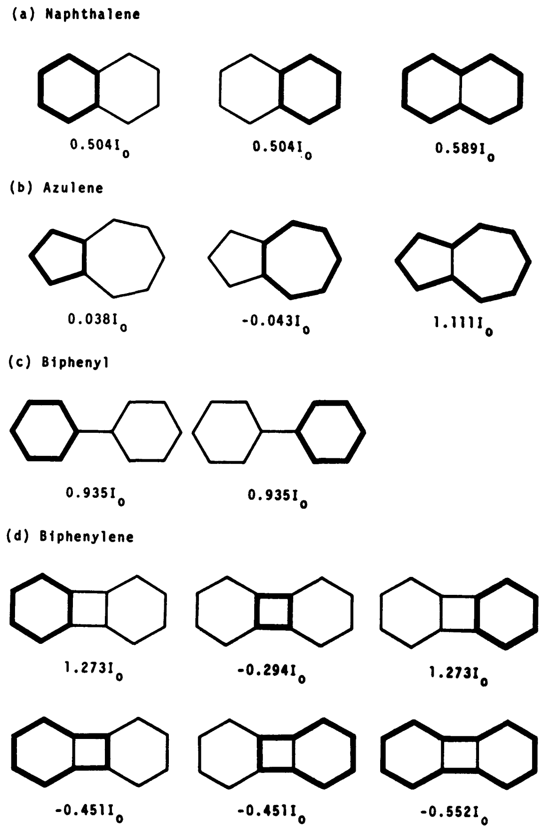

Fig. 1. Constituent π-electron rings and ring currents.

these compounds are structurally combinations of regular polygons with sides equal to a standard carbon-carbon π-bond length. Summing up all ring currents flowing through a given π bond, we obtain an overall current induced there. Overall currents estimated in this manner were found to be exactly the same as those reported by Pople,[10] McWeeny,[13] and Memory.[14] Mathematically, this way of reasoning is identical with that of Pople.[9,10] In this sense, our postulate given as Eq. 5 seems to be quite reasonable. It is to be noted that at the limit of zero field strength ring currents induced in different π-electron rings do not interact with each other, and that the overall current flowing at each π bond is simply an additive sum of individual ring currents defined by Eq. 6.

Salem[9] stated that, for naphthalene and azulene, the central π bond hardly perturbs the annulenic conjugated system formed by the perimeter of ten sp^2-carbon atoms. However, our analysis revealed that the ring current induced in each six-membered ring of naphthalene is comparable in magnitude with that induced in the peripheral ten-membered ring. It is now obvious that the central π bond plays an important role in determining the magnitude of the peripheral current. A weak paramagnetic ring current is predicted along the seven-membered ring of azulene.

In summary, two advantages of our graph theory are that ring currents can be evaluated easily by inspecting the geometry of a cyclic conjugated system, and that they can be assigned uniquely to the individual π-electron rings. We no longer need to expand the field-dependent secular determinant into a polynomial in X and H. The present approach thus presents a novel way of analyzing structural aspects of ring currents and related proton chemical shifts.

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